UDC 666.28:666.29

FLOW PROPERTIES OF SILICATE PAINTS FOR DECORATING GLASS ARTICLES

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Translated from Steklo i Keramika, No. 3, pp. 30 – 32, March, 2004.

The flow properties of turpentine oil, oxyterpene resin solutions, and silicate paints based on them are investigated. It is shown that paints diluted with 20% solution of oxyterpene resin in turpentine have lower viscosity at low shear velocities and more elastic structures. The optimum concentration of silicate paint compositions are determined for each decoration method.

Treating glass articles with silicate paints (colorant mixtures prepared by milling tinted or clear low-melting glasses) contributes to expanding product ranges and improves the exterior appearance of the product [1].

The main component of colorant compositions are film-forming substances (binders) and finely dispersed silica paint powder. The film-forming agents envelope the paint particles, ensuring strong adhesion of film to the surface colored, and form a continuous solid elastic film. Depending on the nature of the binder, paints are grouped into oil paints, where the film-forming agent is turpentine oil, and enamel paints, in which film-forming substances are synthetic resins [2]. At present new efficient binders for silicate paints can be produced by the wood-chemical industry (polyterpenes, oxyterpene resins, oxypolymers, colophony), which make it possible to produce fast-drying enamel coatings with improved parameters [2, 3].

The technological properties of paints, their behavior in painting articles, the quality of a pattern, and the decoration method to a great extent depend on their rheological properties. Therefore, studying flow properties of paints and the factors responsible for these properties, such as the viscosity of the binder and the concentration of the disperse phase in the binder, constitutes an important theoretical and practical problem.

The present study describes the results of studying the rheological properties of turpentine oil, oxyterpene resin solutions in turpentine, and silica paint compositions for glass based on them.

The flow properties were measured on a Reotest-2 set, which is a rotary viscosimeter to determine the viscosity of Newtonian and non-Newtonian liquids in a wide interval of shear velocities (3 – 1312 sec^{-1}) at 30°C. The mechanical effect on suspensions investigated in this case was the rotation of the inner cylinder of the rotary measuring unit of the viscometer. Viscosity values were calculated based on these results.

The dispersion medium was turpentine oil produced by oxidation of oleoresin turpentine by air in an open vessel for several weeks and 5 – 20% solutions of oxyterpene resin (TU 81-05-69–69) in turpentine, whereas the solid-phase filler was a finely milled low-melting green glaze dried at 100 ± 5°C for 1 h with particle size less than 40 μm, whose main components are oxides of silicon, boron, lead, and chromium. Suspensions with a mass content of powdered filler of 10 – 60% were studied.

Turpentine oil and 5% solution of oxyterpene resin at 30°C are non-Newtonian liquids and their viscosity does not depend on shear velocity, whereas 10 – 20% solutions of oxyterpene resin behave as non-Newtonian fluids already at low shear velocities (Fig. 1). The viscosity curves have segment *I* for plastic flow characterized by the flow of a structuring solution with gradual transition to segment *II*, i.e., the flow of anisotropic aggregates oriented under the effect of a mechanical field (Fig. 1, curves *3* and *4*). It can be assumed that macromolecules in diluted solutions are separated from each other, whereas an increased concentration produces systems in which macromolecules are linked by a lattice of hydrogen bonds. The system of intermolecular interactions changes depending on the solution concentration, which is reflected in the flow of solutions in a mechanical field.

As a consequence of experiments, viscosity values depending on the disperse phase content were obtained. Figure 2 shows dependences of the viscosity of powdered paint mixtures in turpentine oil and in 10 – 20% solutions of oxyterpene resin on their content of the solid phase at 30°C and shear velocity of 3 and 81 sec^{-1}. The viscosity of paints diluted in 10 – 20% solutions of oxyterpene resin at low

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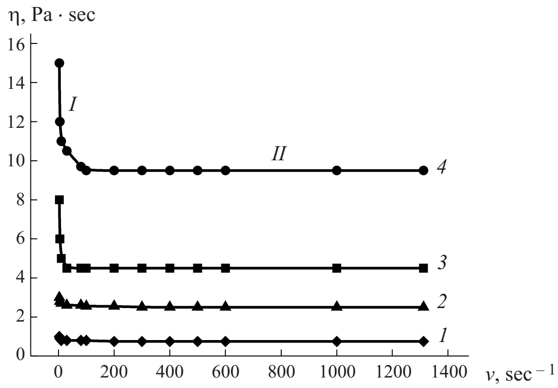

Fig. 1. Dependence of viscosity η on shear velocity v: *1*) turpentine oil; *2*, *3*, and *4*) solutions of oxyterpene resin in turpentine: 5, 10, and 20%, respectively.

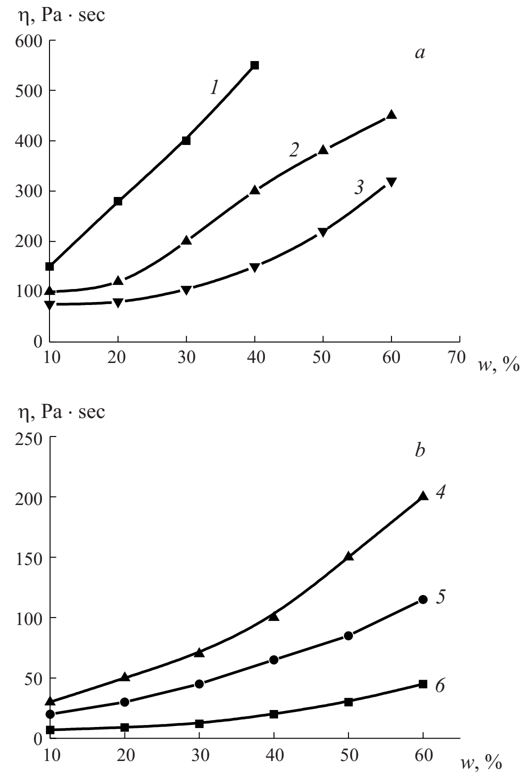

Fig. 2. Dependence of viscosity η of silica paint compositions on solid phase content w for shear velocity 3 sec^{-1} (*a*) and 81 sec^{-1} (*b*): *1*, *6*) turpentine oil, *2 – 5*) solutions of oxyterpene resin in turpentine: 10% (*2*, *5*) and 20% (*3*, *4*).

shear velocities in the beginning grows relatively little. With paint content increasing above 20% thickening becomes more intense. The viscosity of paint diluted in turpentine oil grows sharply at low concentration, i.e., the introduction of the filler into the oil is accompanied by more perceptible thickening than introduction of pulverized paint into oxyterpene solutions. It can be assumed that solvation of viscous oxyterpene solutions stabilizes the solid phase particles and prevents them from aggregation and formation of agglomerates increasing viscosity. This stabilizing capacity of viscous oxyterpene resin solutions is the reason for the relatively lower thickening of paints mixed with them.

Measuring viscosity under the conditions of structure destruction at high shear velocities (for instance, 81 sec^{-1}) we discover that with increasing binder viscosity the viscosity of the paint grows as well. An increased concentration raises the number of contacts of the disperse phase particles per volume unit, which is accompanied by intense structure formation and increasing viscosity.

It can be seen from Table 1 that the viscosity of a non-destroyed structure measured at the shear velocity of 3 sec^{-1} grows with decreasing binder viscosity: the maximum values are registered in the system diluted with turpentine oil.

Thus, with a low viscosity of turpentine oil equal to 1 Pa · sec, the paint viscosity reaches 550 Pa · sec. Paints based on turpentine oil spread unevenly on the surface of the glass article painted and dry poorly. Consequently, tonality of the pattern and luster in decorating articles may vary. Using a 20% solution of oxyterpene resin of viscosity 15 Pa · sec, the paint viscosity is 150 Pa · sec. In paints diluted with viscous 20% solution of oxyterpene resin the structural bonds between the solid phase particles weaken, presumably due to adsorption of the polymer fractions of the resin. These paints have a higher elasticity.

It can be seen in Fig. 3 that pulverized paint mixtures in a 20% solution of oxyterpene resin are non-Newtonian fluids with a marked dependence of viscosity on shear velocity. An increase in the filler content up to 20% leads to increased viscosity at low shear velocities, and the greater the amount of the filler, the higher the viscosity. The viscosity of 20% paint composition in the range of low shear velocities (3 sec^{-1}) typically increases to 80 Pa · sec, that of 40% composition to 150 Pa · sec, that of 50% composition to 220 Pa · sec, and the viscosity of 60% paint to 340 Pa · sec. The viscosity curves in 50 – 60% paint compositions in a 20% solution of oxyterpene resin shift toward greater shear stresses. The effects of anisotropic structure formation in 50% paint are registered at a shear velocity of 300 sec^{-1} and in 60% paint at 500 sec^{-1}.

Each method of decoration requires its particular working consistency and viscosity of paints. Thus, 40% paint

TABLE 1

Binder	Binder viscosity, Pa · sec	Maximum viscosity of non-destroyed structure of mixture with 40% dry paint, Pa · sec
Turpentine oil	1	550
Solution of oxyterpene resin:		
5%	3	420
10%	8	300
20%	15	150

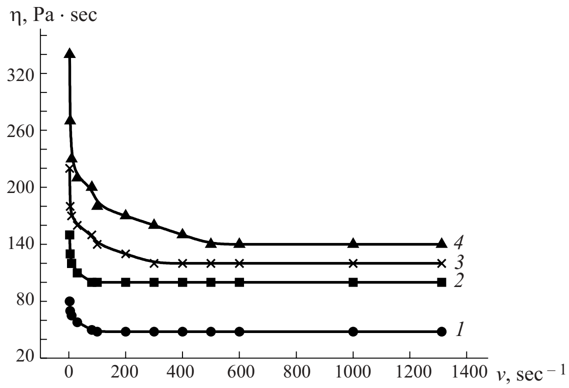

Fig. 3. Dependence of viscosity η on shear velocity *v* of silica paint compositions in 20% solution of oxyterpene resin in turpentine (temperature of the medium 30°C): *1*, *2*, *3*, and *4*) 20, 40, 50, and 60% compositions, respectively.

ought to be used for hand painting of articles and 50% paint for silk-screen printing. When decorating articles with 40% paint, the strokes are uniform and clean, the paint does not spread, dries fast, and has a mirror luster after firing. The 60% oxyterpene mixture of silicate paint can be squeezed onto the article with a special tool, which creates volumetric points that do not change their shape in firing and after treatment with gold produce a volumetric effect.

Analysis of rheological curves of the paints indicates that the less concentrated paint, for instance, the 20% paint (Fig. 3, curve *1*), in contrast to more concentrated ones, has lower viscosity at low shear velocities and, accordingly, better fluidity,. Therefore, an increase in shear velocity is accompanied by a slight modification in their structure, i.e., their viscosity decreases less sharply than in highly viscous paints. This paint can be primarily used for aerography, since paints for the aerography method have to be more fluid than for hand painting. This makes it possible to obtain a uniform coating.

Thus, turpentine oil and 5% solution of oxyterpene resin in turpentine are non-Newtonian fluids and 10 – 20% solutions of oxyterpene resin and paints based on them are characterized by a non-Newtonian behavior.

Modifying turpentine with oxyterpene resin leads to the formation of a medium with plastic properties, which is related to the formation of a lattice of hydrogen bonds in the mechanical field and subsequent (after the shear velocity increases) structuring of the disperse system with formation of anisotropically oriented filler particles.

In contrast to turpentine oil, the 20% solution of oxyterpene resin has better stabilizing capacity. Paints diluted with this solution have lower viscosity at low shear velocities and more elastic structures.

The optimum component ratio of silicate paint compositions has been determined for each decoration method: 20% paints for aerography, 40% for hand painting, 50% for silk-screen painting, and 60% for production of volumetric patterns (points).

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